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The Chemistry of Molybdenum and Tungsten.
Part XII.[1] Molybdenum(V) and Tungsten(V) Complexes of Nitrogen–Sulphur Chelating Ligands. Facile Amine Deprotonations

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The chelating ligands 1,2-di(o-aminobenzenethio)ethane, cis-*1,2-di(o-aminobenzenethio)ethylene, 1,3-di(o-aminobenzenethio)propane and 1,4-di(o-aminobenzenethio)butane react with* $MOCl_3(THF)_2$ *(M = Mo, W) to form the* $[MOCl_3(ligand)]_2$ *complexes in which the ligand is a zwitterion, having transferred a proton from one amine group to the other. The simpler o-aminobenzenethiol reacts with* $MoOCl_3(THF)_2$ *to form* $[MoOCl_3(ligand)_3]$*. E.p.r., infrared and electronic spectra, as well as magnetic moments and conductivity data are discussed.*

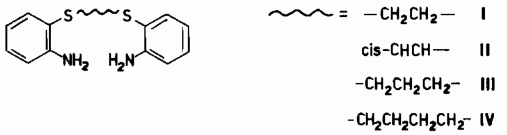
Introduction

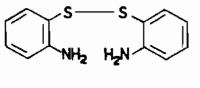
In addition to their widespread industrial uses, molybdenum and tungsten [2] complexes have been shown to be biologically active. The necessity for molybdenum has been established for several enzymes, including xanthine oxidase, aldehyde oxidase, nitrate reductase and nitrogenase [3]. Tungsten is a trace element in formate dehydrogenases of *clostridium thermoaceticum* and *clostridium formicoaceticum* [4, 5].

Recent studies of molybdenum complexes used as enzyme models have concentrated on dimolybdenum complexes which can be cleaved under appropriate conditions to produce the catalytically active monomers [6], and some previous workers have concentrated upon oxo- and thio-bridged oxomolybdenum(V) species [6, 7]. As part of a general study of high-valent molybdenum and tungsten coordination complexes we have discovered a new class of $-NH^-$– bridged species, the synthesis and properties of which are reported here.

Results and Discussion

The ligands used in this study are shown below and their synthesis and properties are given in the Experimental. The reaction of ligands (I)–(V) with $MoOCl_3(THF)_2$ or $WOCl_3(THF)$ (THF = tetrahydrofuran) in toluene/dichloromethane in 1:1 molar ratio results in the immediate precipitation of red or brown microcrystalline molybdenum or blue microcrystalline tungsten complexes, of stoichiometry $MOCl_3 \cdot L$, Table I. Ligand (VI), *o*-aminobenzenethiol, reacts with $MoOCl_3(THF)_2$ to give the black solid $[MoOCl_3(VI)_3]$ ½THF.





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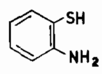

VI

Some important bands from the infrared spectra of the complexes are listed in Table II. In addition to these it can be pointed out that broad absorptions at 3050, 2550, 1610, and 1550 cm^{-1} are present which are assignable to N–H stretching and bending modes of an $-NH_3^+$ group [8]. All the complexes exhibit a strong ν(M=O) vibration in the 970–985 cm^{-1} (Mo) and 960–975 cm^{-1} (W) regions, assignable to terminal metal–oxygen bonds [9, 10]; there is no evidence for bridging M–O–M species. A number of M–Cl stretching bonds are observed, Table II. All of the complexes contain uncoordinated THF [11], as evidence by bonds assignable to (C–O–C) vibrations. Finally, the aromatic C–H out-of-plane bending, which

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TABLE I. Analytical and Physical Data for the Complexes.

Complex	Colour	Found (Calculated)				
		%C	%H	%N	%Cl	%M[a]
[MoOCl$_3$(I)]½THF	Reddish brown	36.1 (36.2)	3.6 (3.8)	5.2 (5.3)	20.1 (20.0)	18.4 (18.1)
[MoOCl$_3$(II)]THF	Dark brown	39.3 (38.3)	3.6 (3.9)	4.4 (4.9)	19.8 (18.8)	16.3 (16.9)
[MoOCl$_3$(III)]THF	Reddish brown	39.1 (39.3)	4.1 (4.5)	5.3 (4.8)	18.4 (18.3)	16.8 (16.5)
[MoOCl$_3$(IV)]½THF	Orange brown	38.0 (38.7)	4.2 (4.3)	5.2 (5.0)	20.4 (19.0)	16.7 (17.2)
[MoOCl$_3$(V)]THF	Reddish brown	36.3 (35.7)	3.4 (3.7)	6.0 (5.2)	19.5 (19.7)	17.7 (17.8)
[MoOCl$_3$(VI)$_3$]½THF	Grey black	39.4 (38.0)	3.9 (4.0)	7.2 (6.7)	17.0 (16.9)	13.6 (15.2)
[WOCl$_3$(I)]½THF	Blue grey	30.6 (31.1)	3.5 (3.3)	4.8 (4.5)	16.9 (17.2)	29.4 (29.7)
[WOCl$_3$(II)]½THF	Mid blue	29.3 (31.2)	2.8 (2.9)	4.6 (4.5)	16.9 (17.2)	30.0 (29.8)
[WOCl$_3$(III)]½THF	Blue grey	30.9 (32.3)	3.6 (3.5)	3.5 (4.4)	17.5 (16.8)	31.1 (29.1)
[WOCl$_3$(IV]½THF	Blue grey	32.5 (33.4)	3.7 (3.7)	4.0 (4.3)	16.2 (16.4)	28.6 (28.4)
[WOCl$_3$(V)]½THF	Dark blue	27.8 (28.5)	2.8 (2.7)	4.4 (4.7)	16.3 (18.0)	31.1 (31.1)

[a] M = Mo or W.

TABLE II. Physical and Spectral Data for the Complexes.

Complex	Infrared Data (cm^{-1})[a]			μ_{eff} (BM) room temp.	Λ_M/DMF ($^{-1}$ mol^{-1} cm^2)
	ν(M=O)	ν(M–Cl)	ν(COC)		
[MoOCl$_3$(I)]½THF	985	375(w), 315(b)	1080(s)	1.24	36
[MoOCl$_3$(II)]THF	980	315(b)	1074(m)	1.23	32
[MoOCl$_3$(III)]THF	975	350(b), 290(b)	1075(m)	1.10	46
[MoOCl$_3$(IV)]½THF	985	375(w), 315(b)	1075(s)	1.20	38
[MoOCl$_3$(V)]THF	980	375(vw), 315(b)	1075(vw)	1.20	40
[MoOCl$_3$(VI)$_3$]½THF	970(s)/980(sh)	390(s), 330(m), 280(m) (b)	1075(s)	1.69	39
[WOCl$_3$(I)]½THF	975	380(sh), 310(b)	1080(s)	1.14	33
[WOCl$_3$(II)]½THF	970	370(bsh), 315(b)	1075(s)	1.03	31
[WOCl$_3$(III)]½THF	975		1075(s)	0.91	43
[WOCl$_3$(IV)]½THF	970	370(bsh), 310	1075(s)	0.93	39
[WOCl$_3$(V)]½THF	975	370(b), 310	1075(s)	0.88	36

[a] s = sharp, b = broad, w = weak, vw = very weak, sh = shoulder, m = medium.

appears as a single band *ca.* 760 cm^{-1} in the spectra of ligands (I)–(V), is split into a doublet (760 and 730 cm^{-1}) in all the complex spectra. This may suggest different orientations of the aromatic system in the complexes as compared to those in the ligands.

The electronic spectra of the complexes are listed in Table III. In the visible region two main absorptions occur, at *ca.* 21 kK and *ca.* 13.5 kK. The former is usually assigned to the $^2B_2 \rightarrow {}^2B_1$ ligand field transition in complexes of octahedral symmetry and the latter to the $^2B_2 \rightarrow {}^2E_1$ transition involving the π-orbital of the oxygen atom [12]. The spectra are broadly similar in the solid state and in DMF solution, indicating a similar coordination environment in both physical states. Complex solutions in DMF are not sufficiently stable for accurate extinction to be calculated.

The molar conductivities, Λ_m, are listed in Table II. These measurements were obtained on freshly prepared solutions in DMF and, since these solutions do deteriorate with time, some care must be taken in assessing the results obtained. Repeated measurements, however, do lead us to believe that the values obtained are approximately one-half of those expected for 1:1 electrolyte systems in DMF [13]. The room-temperature magnetic moments are also listed in Table II and are significantly lower than those expected for d^1 systems. We have obtained magnetic measurements over the temperature range 98–293 K for [MoOCl$_3$(III)] and the results are plotted in Figure 1. Although the plot of χ_m *versus* T obeys the Curie law for simple paramagnetism the plot of the reciprocal of χ_m *versus* T does not yield a straight line covering all the range of temperature. One

TABLE III. Electronic Spectra of the Complexes.

Complex	Reflectance Spectra (kK)[a]				Solution Spectra (kK)[a,b]			
[MoOCl$_3$(I)]½THF	20.9(s)	13.7(b)			13.0	21.3	26.3(sh)	32.3
[MoOCl$_3$(II)]THF	20.9(s)	13.0(b)			13.0	21.3		32.3
[MoOCl$_3$(III)]THF	20.8(s)	13.5(b)			13.0	21.3		32.5
[MoOCl$_3$(IV)]½THF	20.8(s)	31.5(b)			14.0	21.3		32.2
[MoOCl$_3$(V)]THF	20.8(s)			12.5	13.2	21.9		32.3(sh)
[MoOCl$_3$(VI)$_3$]½THF	21.9	17.0		12.5	14.7		29.0	32.8(sh)
[WOCl$_3$(I)]½THF	21.7(sh)	16.8	14.1	11.6	13.0	14.9		32.3
[WOCl$_3$(II)]½THF		16.8	14.1	11.6	13.3		27.sh	32.3
[WOCl$_3$(III)]½THF	21.7(sh)	16.9	14.3	11.9	13.2	15.2		32.3
[WOCl$_3$(IV)]½THF	21.3(sh)	16.9	14.3		15.0 (650)	17.4 (610)	27.0 (400)	32.6 (8350)
[WOCl$_3$(V)½THF		17.5	14.0	11.4	13.8	16.9	28.6	

[a] s = sharp, b = broad, sh – shoulder. [b] In DMF.

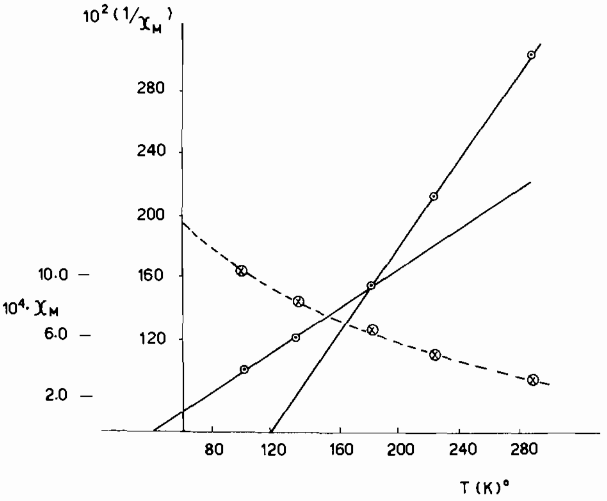
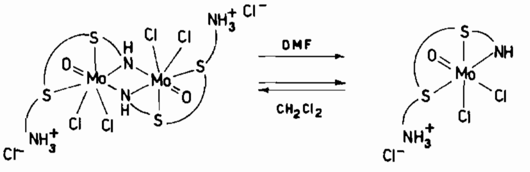


Figure. Plot of χ_M *vs.* T for [MoOCl$_3$(III)].

straight line gives a value of θ = 42K and the other gives θ = 98K. The results do not provide direct evidence for antiferromagnetic exchange interaction between bridged metal ions, but such exchange is not ruled out provided the coupling constant is large.

Data obtained from e.p.r. spectra are listed in Table IV. The general aspects of the [MoOCl$_3$(ligand)] spectra in dichloromethane is as follows; there is a major signal with superhyperfine structure at g ~1.96 and a smaller signal at g ~ 1.950. Over a period of one hour both of these signals decrease in magnitude and a new signal grows at g ~1.939; this corresponds to a lightening in colour of the solutions and is probably due to some decomposition. The major signal shows a partially resolved (1:1:2:1:2:1:1) septet due to coupling to two non-equivalent nitrogens with A(^{14}N) ~ 5G and ~ 2.5G, while the g ~ 1.950 signal shows a (1:1:1) triplet due to superhyperfine coupling to a single nitrogen with A(^{14}N) ~ 5G. In the presence of 1% of DMF only the g ~ 1.950 signal is observed. The use of the deuterated ligand, (o-$D_2NC_6H_4SCH_2)_2$, does not change the superhyperfine coupling pattern, confirming that it is ^{14}N and not ^{1}H coupling [14]. The e.p.r. data, in conjunction with the infrared results mentioned earlier, leads us to believe that the major signal can be assigned to the dimeric species (A) and the g ~ 1.950 signal to the monomer (B):



A B

The results for the tungsten complexes are not so readily interpretable, because lack of sufficient solubility did not allow for studies in dichloromethane. Nonetheless, in DMF it is likely that the monomeric type (B) is present. The postulation of the existence of zwitterionic ligands is not only in keeping with the strong evidence for $-NH_3^+$ present in the infrared spectra, but also explains the conductance properties due to the presence of the ammonium salts.

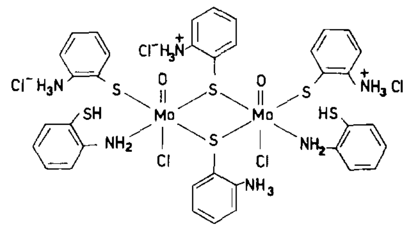
Only the [MoOCl$_3$(VI)$_3$]½THF exhibits a magnetic moment near the spin-only value, Table II. The infrared spectrum of this complex shows evidence for $-NH_3^+$ and also for the presence of unionised thiol groups. The ν(Mo=O) vibration also contains a shoulder at slightly lower energy. This may be due to the presence of two slightly different molybdenum environments, or be due to crystal packing forces. The room-temperature e.p.r. spectrum of this complex shows a single signal at g = 1.964 with

TABLE IV. Electron Spin Resonance Data for the Complexes

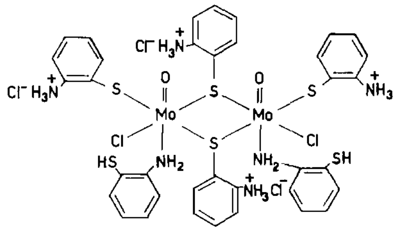
Compound	CH_2Cl_2			DMF			Solid powder	Frozen solution
	g_{iso}	A_{iso} (^{95,97}Mo)G	A(^{14}N)G	g_{iso}	A_{iso} (^{95,97}Mo)G	A(^{14}N)G		
[$MoOCl_3$(I)]½THF	1.959	50		1.949	55	5(1:1:1)t	1.980, 1.950, 1.930	
	1.949							
[$MoOCl_3$(II)]THF	1.953	52	5(1:1:1)t	1.949	52	5(1:1:1)t		
[$MoOCl_3$(III)]THF	1.960	50	2.5(1:1:2:1:2:1:1)s	–	–	–		
[$MoOCl_3$(IV)]½THF	1.962	–	5(1:1:1)t					
	1.945		2.5(1:1:2:1:2:1:1)s	–	–	–		
[$MoOCl_3$(V)]THF	1.947	–		1.947	53	5(1:1:1)t		
[$MoOCl_3$(VI)$_3$]½THF	1.964	48		1.960	48	A (^{14}N), 2, A(^{1}H) 1 (1:1:1:2:2:2:1:1:1)^b		
[$WOCl_3$(I)]½THF	1.794			1.746	5(1:1:1)t^a			1.79, 1.74, 1.71
[$WOCl_3$(II)]½THF	c			1.746	5(1:1:1)t^a			
[$WOCl_3$(III)]½THF	c			1.746	5(1:1:1)t^a			
[$WOCl_3$(IV)]½THF	c			1.750	5(1:1:1)t^a			1.833
								1.789
[$WOCl_3$(V)]½THF	c			1.748	5(1:1:1)t^a			1.707

[a] Not well resolved. [b] At –33 °C. [c] Insufficient solubility.

A(^{95,97}Mo) = 48G. Addition of one drop of DMF to this solution produces a similar single peak at g 1.960 with A(^{95,97}Mo) = 48G. On cooling the solution to –33 °C the signal resolution becomes sharper and hyperfine structure of a (1:1:1:2:2:2:1:1:1) pattern is observed when the spectrum is recorded as a double derivative. This pattern may be interpreted in terms of coupling of an $-NH_2$ group with A(^{14}N) ~ 2G and A(^{1}H) ~ 7G. On the basis of the e.p.r. and infrared spectral evidence the bridging dimeric structures (C) or (D) are possible.



C



D

It is noteworthy that only in the cases of $MOCl_3(THF)_2$ (M = Mo, W) do we observe this facile amine deprotonation of the ligands to yield the $-NH^-$ and $-NH_3^+$ groups; in our studies on other metal salts, *e.g.* Co(II), Ni(II), Pd(II), Pt(II), Rh(III), we observe simple tetradentate behavior [15].

Experimental

The solvents used were dried by distillation from sodium benzophenone ketyl or, in the case of dichloromethane, from molecular sieves. All preparations were conducted under a dry nitrogen atmosphere using standard Schlenk tube and drybox techniques. Physical measurements were made as described previously [16]. E.p.r. spectra were obtained on a Varian E9 E.P.R. spectrometer using the dual cavity mode and were run in the X-band (~9.3GH$_2$) in CH_2Cl_2 or DMF at various temperatures +35 to –160 °C. The ligands were prepared by the general method detailed below.

1,2-Di(o-aminobenzenethio)ethane

Approximately 250 ml of dry ethanol was transferred into the 500 ml round bottomed flask. Ethanol was then deoxygenated by bubbling with dry nitrogen gas for about 2 hours. 7 g (0.304 mol) of dry sodium metal were added slowly to ethanol with constant stirring under a steady flow of nitrogen. When the vigorous reaction has subsided, the reaction mixture was warmed in an oil bath until all the sodium had reacted, and then allowed to cool down to room temperature.

Approximately 70 ml of practical grade *o*-aminobenzenethiol (yellow liquid b.p. 234 °C) were distilled under reduced pressure using an oil pump. The colourless fraction boiling at 90 °C/0.3 mmHg was collected (oil bath temperature 107 °C). 37.5 g (0.3 mol) of this fraction were transferred rapidly into a pressure equalized dropping funnel and added slowly to the colourless ethoxide solution. The reaction mixture was refluxed for about 1 hour and then allowed to cool down to room temperature.

A freshly distilled 1,2-dibromoethane (28.2 g, 0.15 mol) of b.p. 130 °C was added dropwise to the colourless reaction mixture of the sodium salt of *o*-aminobenzenethiol. When the addition of the dihalide was complete (*ca.* 45 minutes), a white solid separated out from a very pale yellow solution. The solid precipitated almost immediately after the addition of most of the dihalide, but stirring under nitrogen at room temperature was continued for a further 24 hours.

Distilled water (*ca.* 200 ml) was added to the reaction mixture, and the contents of the flask were transferred into a one litre separating funnel. The product was extracted with three 100 ml portions of ether. The ether was then evaporated off from the combined ether extracts using a rotary evaporator. The residual white solid was then dissolved in boiling methanol (*ca.* 200 ml). Methanol solution was cooled in air and then diluted with water until all the solid separated out. After cooling in ice, the solid was filtered off, washed with small amount of cold methanol/water mixture and then dried in a vacuum dessicator over calcium chloride. Yield = 96% based on the dihalide.

An alternative method for the isolation and purification of the product is as follows: cool the mixture of the white solid and the very pale yellow solution, and filter off the solid. Dissolve the solid in a hot methanl/water mixture (*ca.* 3:1 v/v) and heat until the mixture turned colourless. Cool in air then in ice and filter off the solid product. Add more water if no solid precipitated on cooling in ice.

The Metal Complexes

A pre-weighed sealed ampoule of the $MOCl_3(THF)_2$ (M = Mo, W) reagent was broken against a flow of nitrogen and the constants transferred immediately into a dropping funnel containing 60 ml CH_2Cl_2. This was then slowly added to a solution of the ligand (1:1 molar ratio) in toluene/CH_2Cl_2. Reaction occurred at once and the resulting precipitate was stirred for 30 minutes. The solid was filtered off by Schlenk tube techniques, washed with n-pentane and dried under vacuum.

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